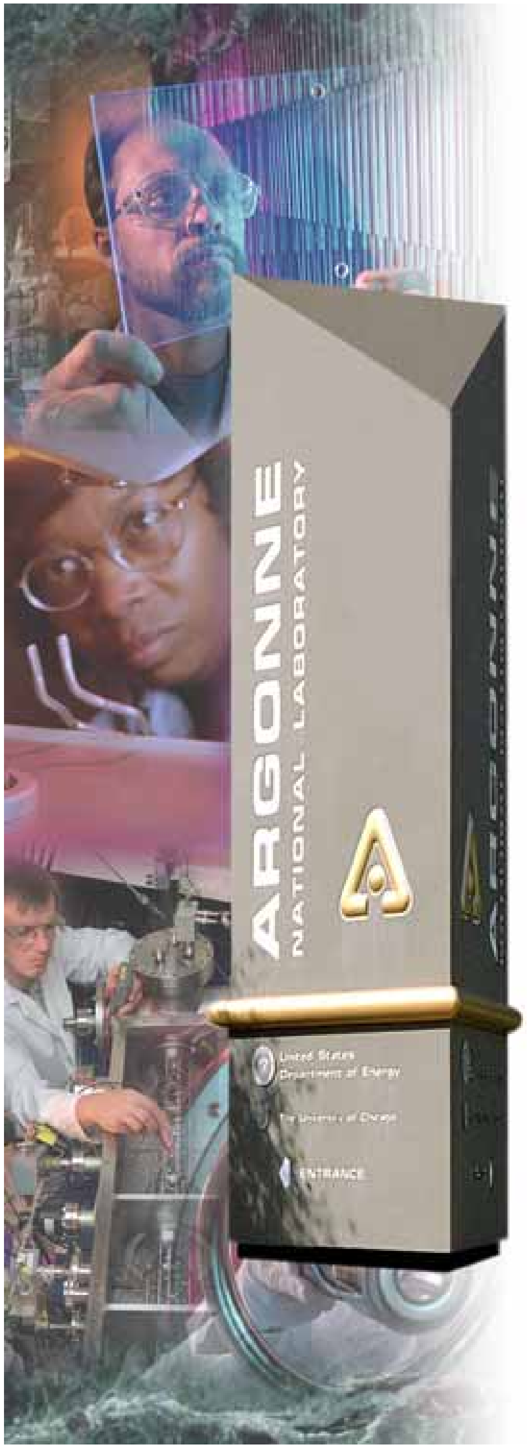

Critical Issues in Catalytic Diesel Reforming for Solid Oxide Fuel Cells

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ASM Materials Conference & Show
Columbus, OH
Oct. 18-21, 2004

Argonne National Laboratory

Office of Science
U.S. Department of Energy

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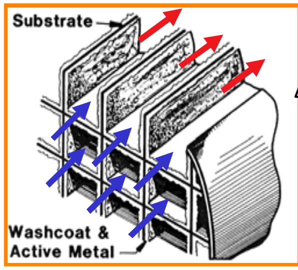
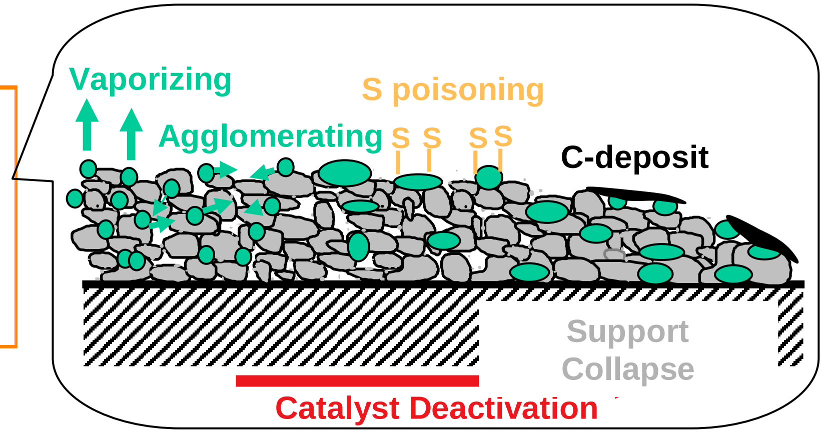
The Critical Issues in Diesel Reforming Catalyst & Catalytic System Development

Catalyst

- Cost
  - Costly Rh usage
- Activity
  - ATR, POX or SR?
  - Efficiency & Selectivity
  - Fuel property & chemistry
- Durability
  - Metal vaporization & agglomeration
  - Support stability
  - Sulfur poisoning
  - Coke formation

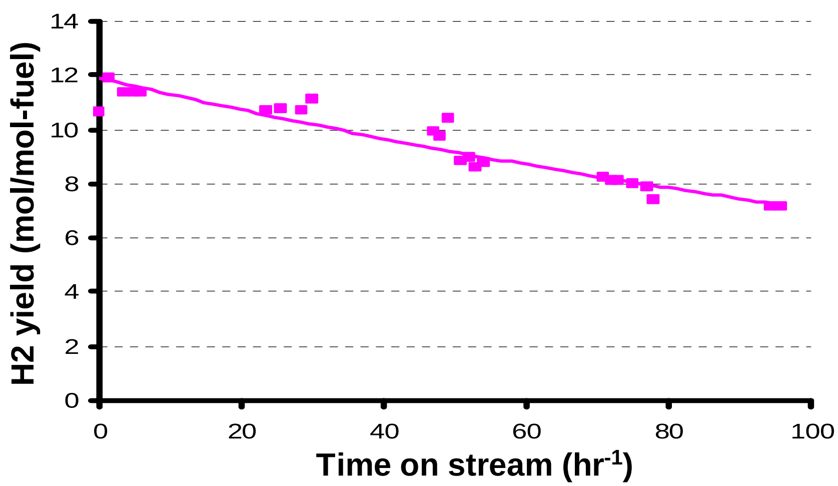




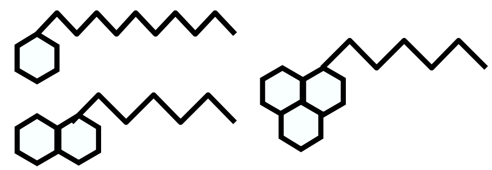
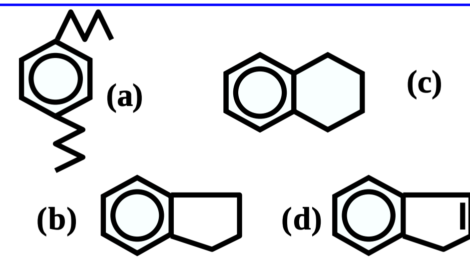
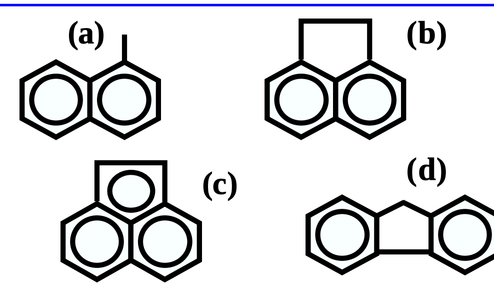
System

- Fuel injection & mixing
- Reactor components
- System integration

Reforming catalyst aging – an example



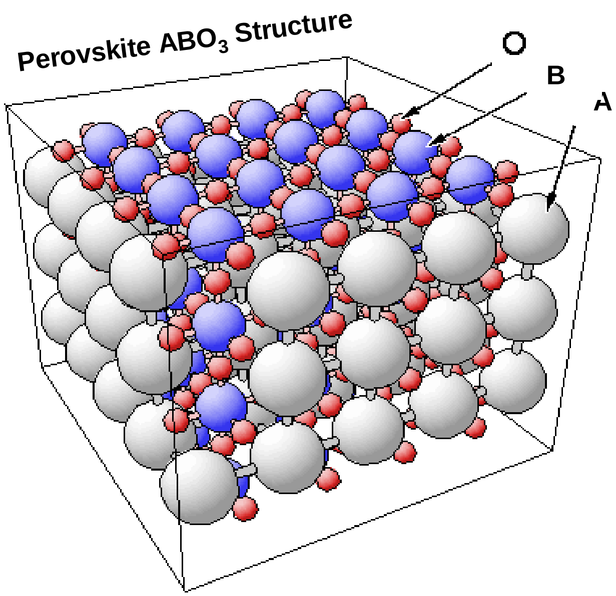
Examples of Diesel Hydrocarbon Components

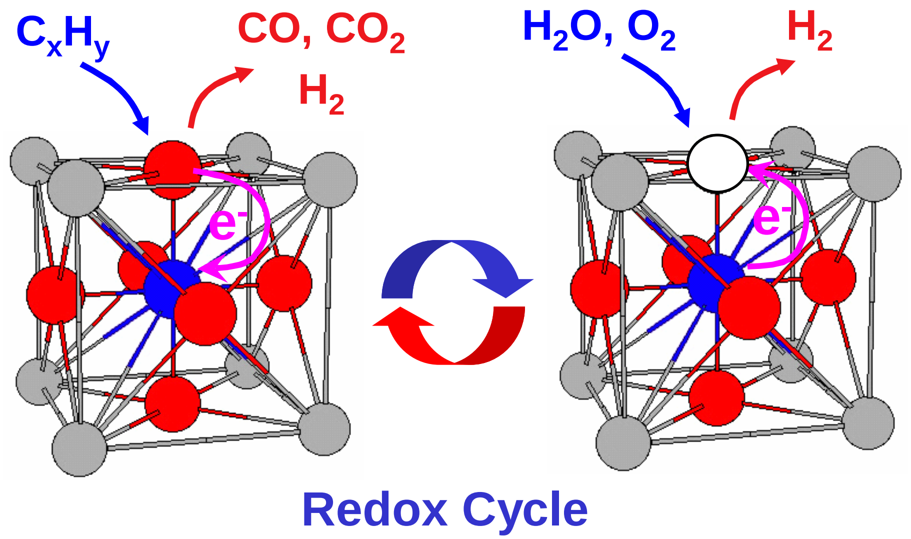
Compound Type	Wt% Analysis, ANL	Wt% Analysis, Exxon	Ave. or Ref. Formula (ANL)	Representative Molecular Structures
Paraffins	38.7	39.7	$C_{16}H_{34}$	
Cycloparaffins 1-ring cycloparaffins 2-ring cycloparaffins 3-ring cycloparaffins	 29.6 11.5 4	 23.6 20.6 6.5	 $C_{10}H_{21}$ $C_{16}H_{32}$ $C_{22}H_{38}$	
Mono-aromatics Alkyl benzenes (a) Naphthenebenzenes (Indans (b) + Tetralins (c) + Indens (d))	 7.3 3.2	 3.2 0.9	 C_8H_8 $C_{12}H_{16}$	
Di-aromatics Alkylnaphthalenes (a) Acenaphthenes (b)/Biphenyls Acephthalenes (c)/Fluorenes (d)	 1.8 3.5 0.3	 1.6 2.2 1.7	 $C_{13}H_{14}$ C_9H_{12} $C_{13}H_{10}$	

Diesel Reforming Catalyst Development

Approach: Development of Perovskite Based Catalyst

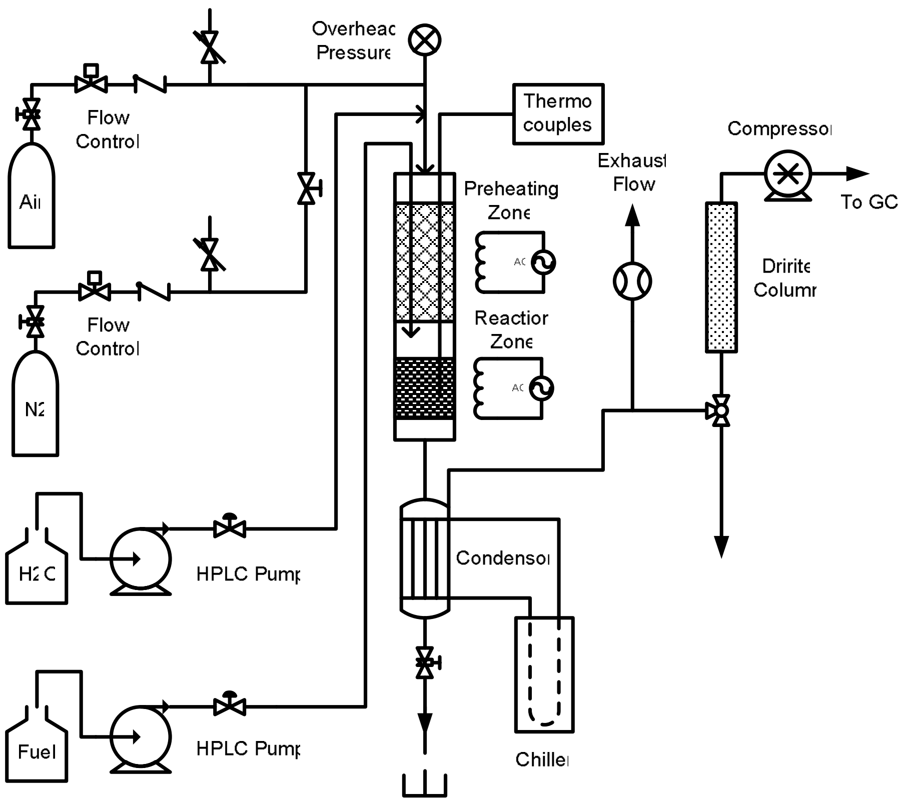
- **The Perovskite Catalyst…**
  - Low cost material.
  - Stable under high temperature & redox environment.
  - Exchangeable *A & B* site for activity improvement & metal dispersion.





Conductivities of both e^- and O^{2-} of perovskite expand the catalytic active site through electron and oxygen vacancy transfers in a redox process.

Diesel Catalyst Development: Test Apparatus & Conditions



Diesel Reforming Catalyst Test Plant

- **Fuel**
  - **Dodecane $C_{12}H_{26}$**
  - **Dodecane/Dibenzothiophene (50 ppm S)**
  - **Dodecane/1-Methylnapthlene (5%)**
- **Catalyst**
  - **Ru doped Chromite & Aluminite**
  - **Combustion method**
- **Microreactor**
  - **Temperature: 700 °C to 800 °C**
  - **Preheating: 200 °C**
  - **GC analysis for reformate products**
- **Reforming Input Mixture**
  - **ATR: O_2/C = 0.3 ~0.5, H_2O/C = 1 ~ 3**
- **Space Velocity**
  - **Fuel Flow Rate = $2.8x10^{-3}$ gfuel/gCat•sec**
  - **GHSV = 50 K ~ 100 K hr^{-1}**

Diesel Catalyst Development: Test Plant

Diesel ATR Catalyst Development – H_2 Yield and COx Selectivity of Some Representative Samples

Definition:

H_2 yield = C_{H2} / C_{fuel}

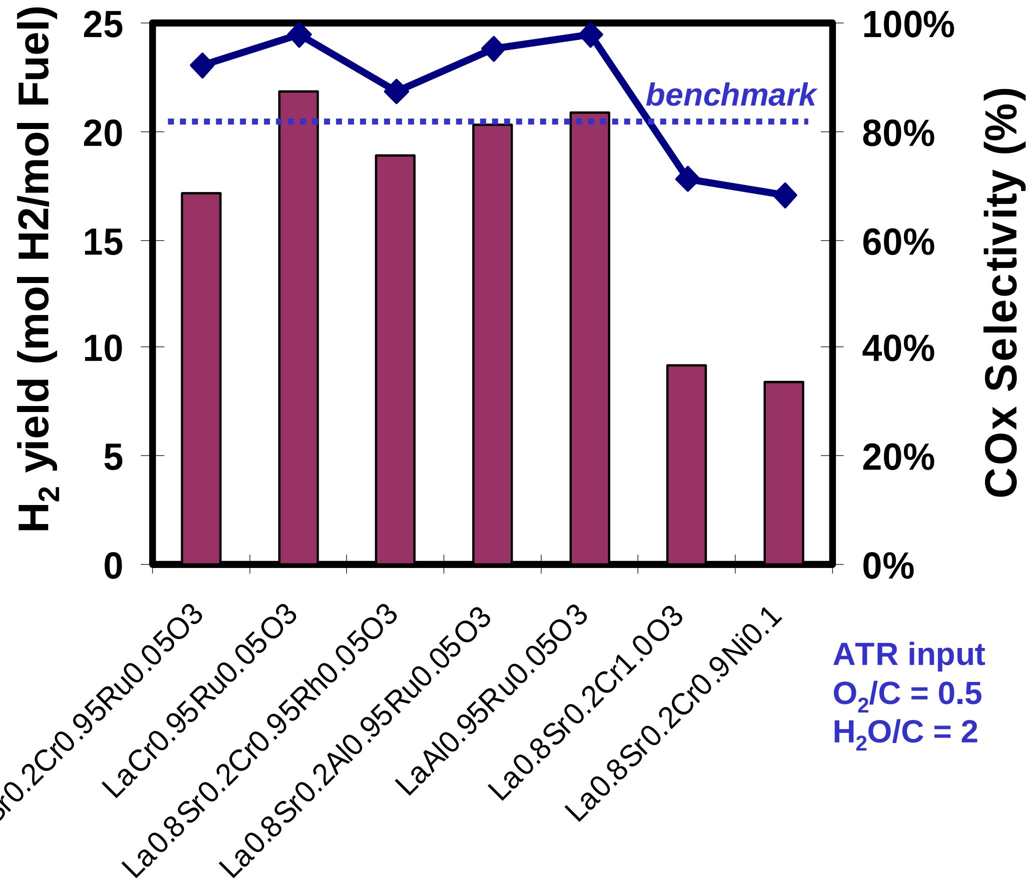
Reforming efficiency =

$\{C_{H2}\Delta Hc_{H2} + C_{CO}\Delta Hc_{CO}\} / C_{fuel}\Delta Hc_{fuel}$

COx selectivity =

$\{C_{CO2} + C_{CO}\} / nC_{fuel}$

C_i = Molar flow of *i*,
ΔHc_i = Heat of combustion of *i*,
***n* = Number of C in fuel molecule**

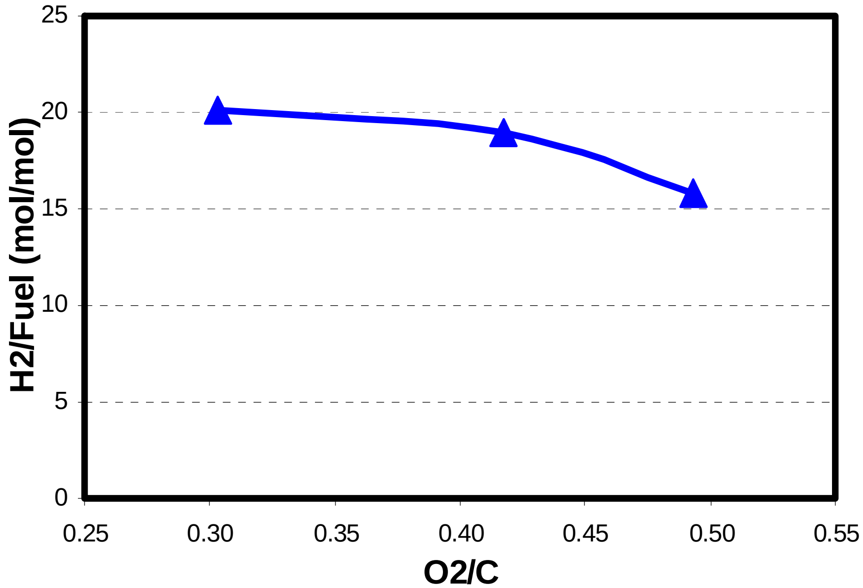


ATR input
$O_2/C = 0.5$
$H_2O/C = 2$

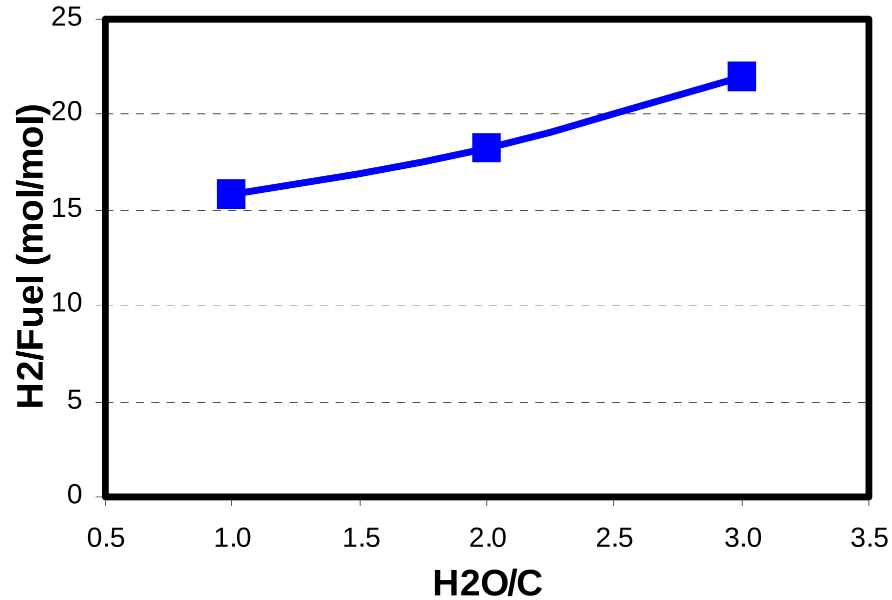
$$C_{12}H_{26} + 6O_2 + 12H_2O = 12CO_2 + 25H_2$$

Diesel ATR Catalyst Development – H_2 Yield as Function of O_2/C and H_2O/C

The hydrogen yield as the function of O_2/C during the reforming over $La_{0.8}Sr_{0.2}Cr_{0.95}Ru_{0.05}O_3$, $H_2O/C = 1.0$



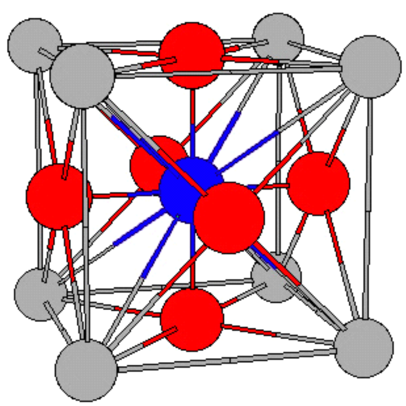
The hydrogen yield as the function of H_2O/C during the reforming over $La_{0.8}Sr_{0.2}Cr_{0.95}Ru_{0.05}O_3$, $O_2/C = 0.5$



Ru doped chromite and aluminite are also excellent steam reforming catalysts!

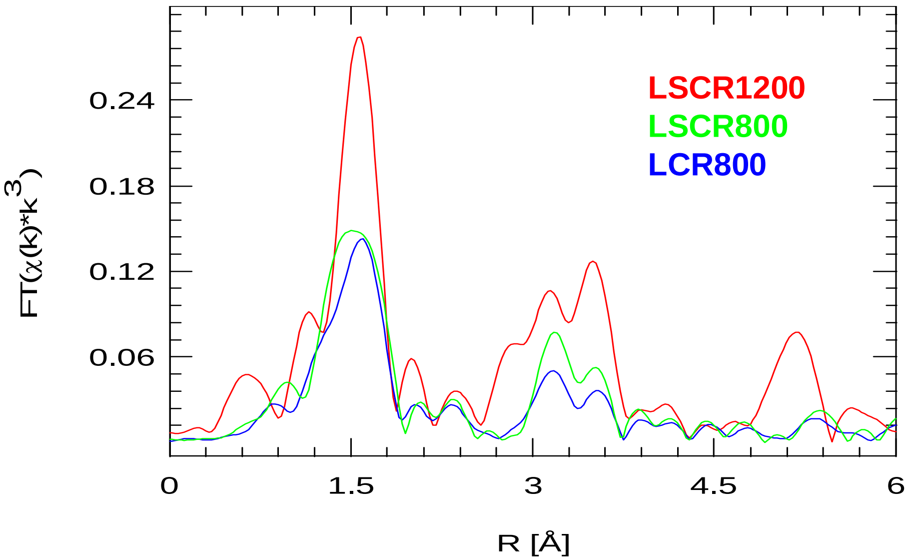
Diesel ATR Catalyst Development – Optimize Activity through Synthesis & Characterization

- **Forming highly dispersed active site through self-combustive powder formation method.**
- **Modification of redox behavior and lattice structure through *A* & *B* site substitution.**
- **Improve catalytic surface area and activity through calcination temperature.**



Lattice Structure of a Single Cell in Perovskite

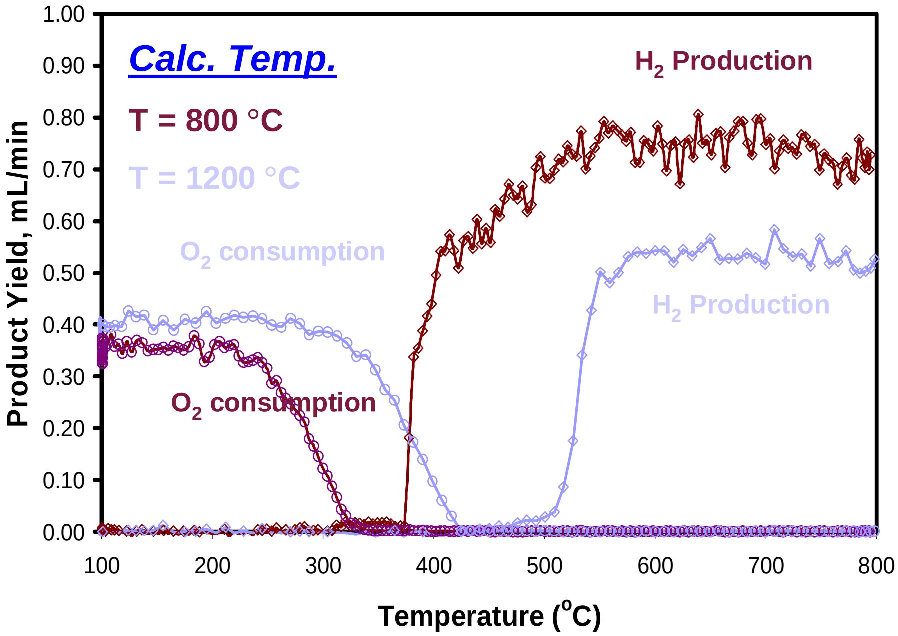
EXAFS analysis on Ru in chromite identified structural difference for catalysts prepared under different condition



	N	*R (Å)*	σ^2
LCSR1200	6.0	1.943	$2.5x10^{-5}$
LCSR800	4.7	1.953	$2.5x10^{-5}$
LCR800	4.3	1.962	$1.0x10^{-5}$

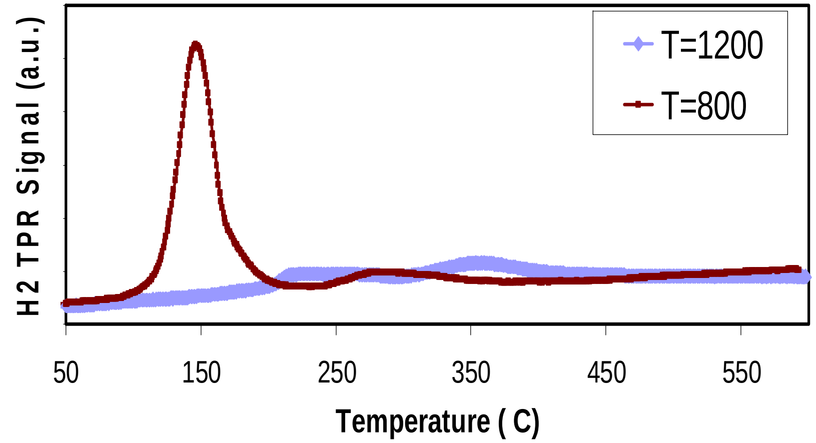
Diesel ATR Catalyst Development – Optimize Activity through Synthesis & Characterization

Catalyst prepared at lower calcination temperature improved reforming lightoff threshold…



Study on ATR lightoff temperature for isobutane

Combined TPR and BET studies suggest the reduction of Ru at perovskite surface attribute to catalytic reaction.



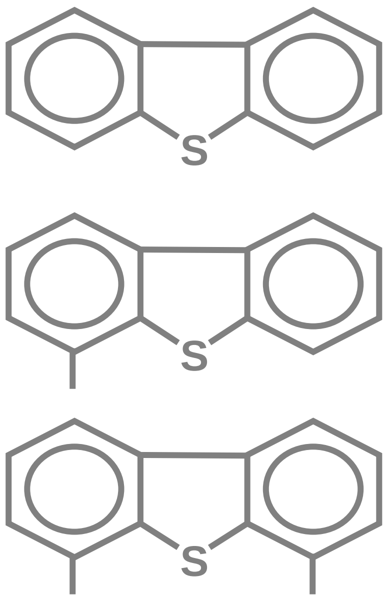
Sample	*LSCR-1200*	*LSCR-800*	*LCR-800*
BET Area (m^3/g)	3.10	18.3	21.6

- **Ru imbedded near perovskite surface via lattice defects is the active site.**
- **Redox mechanism involves Ru^{+3} to Ru^{0} transition.**

Diesel ATR Catalyst Development – Investigation on Sulfur Catalytic Poisoning

Dibenzothiophene (DBT) and its derivatives are difficult to be removed from diesel through HDS process …

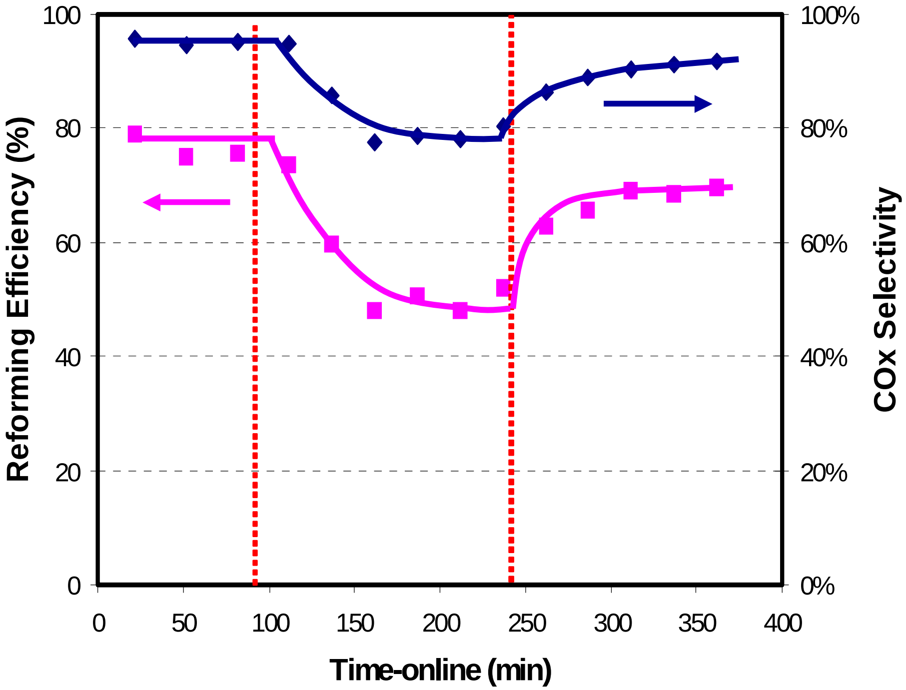
Introducing 50 ppm sulfur in the form of DBT temporarily suppress reforming efficiency and COx selectivity.



DBT

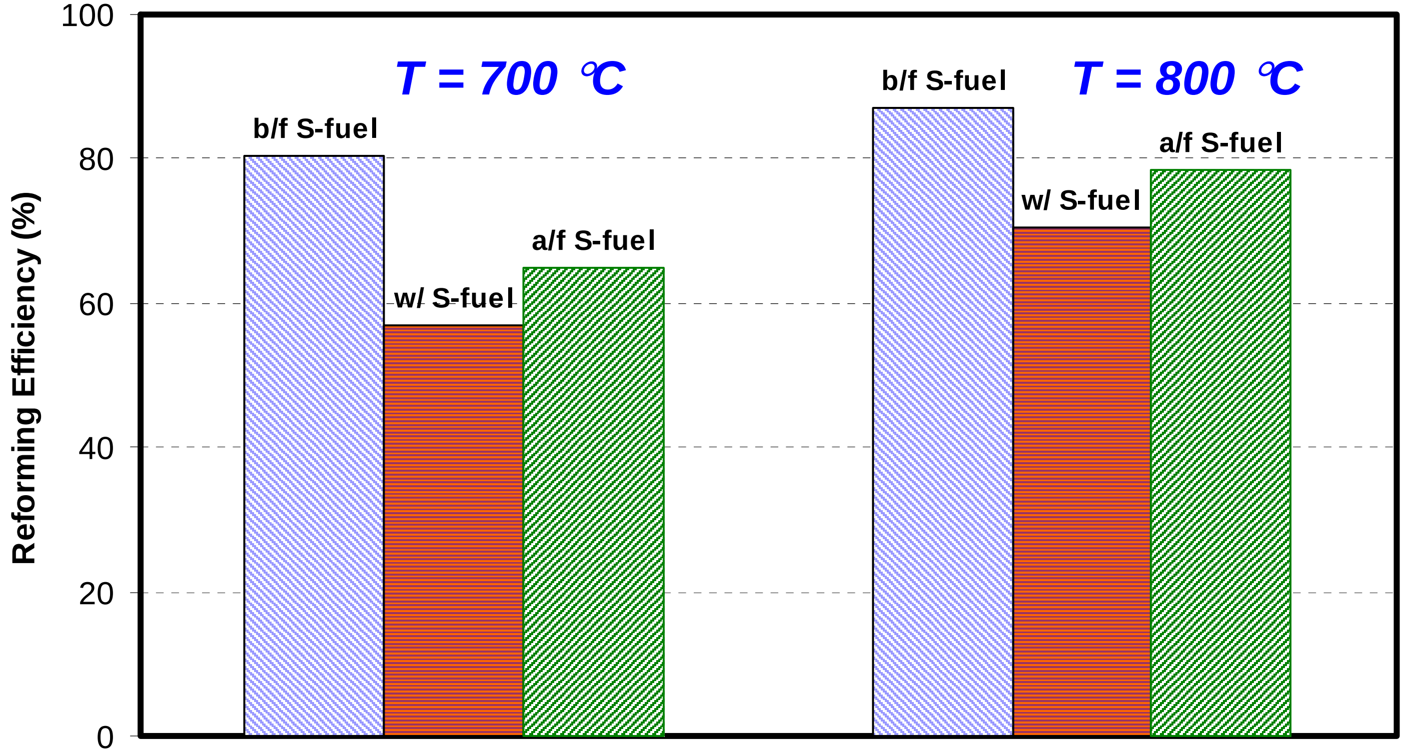
4-MDBT

4,6-DMDBT



Catalyst re-activates after S is removed from fuel.

Diesel ATR Catalyst Development – Impact of Sulfur Tolerance at Higher Operating Temperature

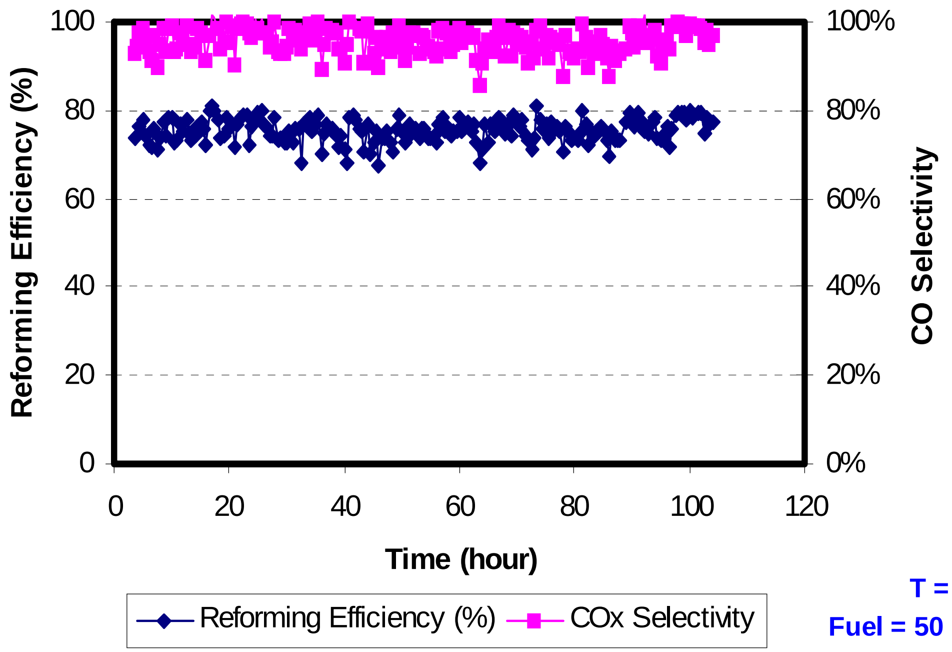


Catalyst = LCR-800, O_2/C = 0.5, H_2O/C = 1.0, GHSV = 130,000 hr^{-1}

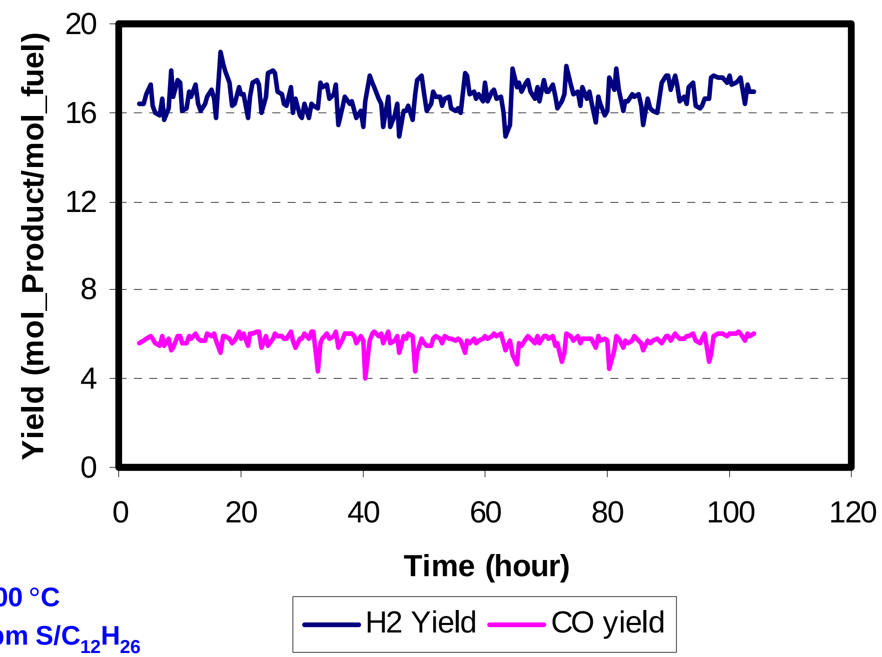
Increase reaction temperature by 100 °C significantly improved catalytic performance in the presence of sulfur

Diesel ATR Catalyst Development – 100 Hr Aging Test in the Presence of Sulfur

Little changes observed in reforming efficiency and COx selectivity throughout the test…



Yields of hydrogen and carbon monoxide (both are SOFC fuels) also maintained constant during the study.

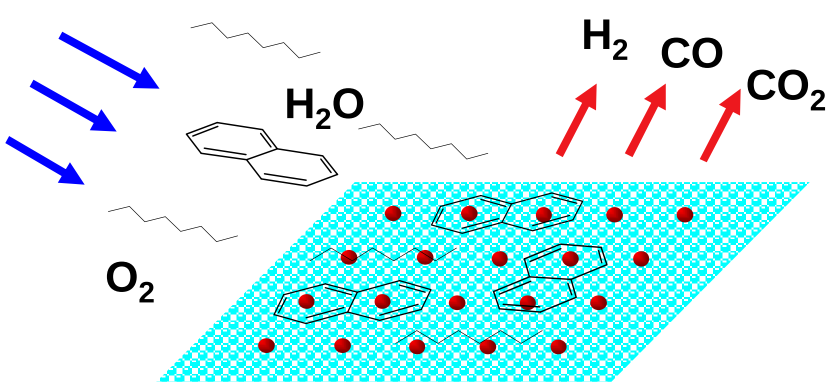


T = 800 °C
Fuel = 50 ppm S/$C_{12}H_{26}$
GHSV = 50,000 hr-1

Excellent catalytic stability was observed during 100 hour aging test with S contaminated fuel

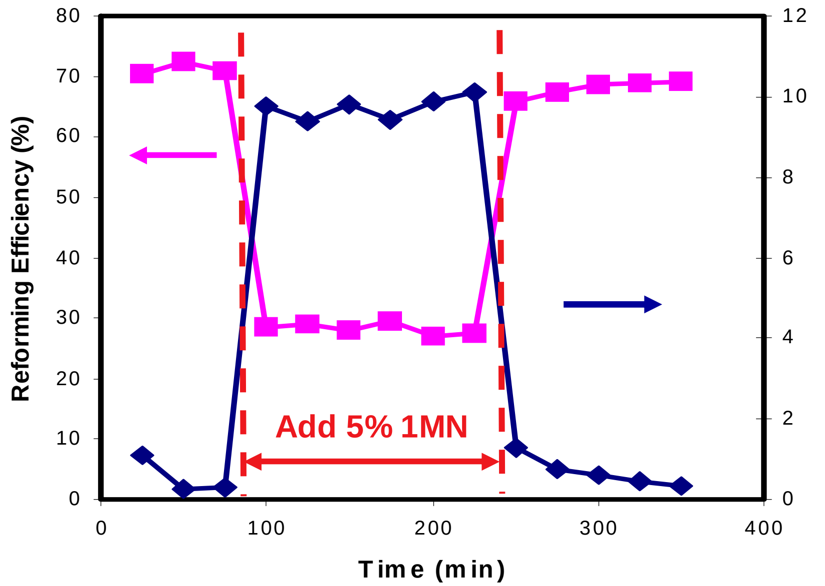
Diesel ATR Catalyst Development – Investigation on Deactivation by Polyaromatics

- **Challenges of PAH in Diesel Reforming**
  - Low cetane number
  - Low ignition temperature
  - Cause for carbon formation
  - Difficult to reform



Long resident time and slow decomposition of PAH over active site reduce reaction rate!

- **Impact on ATR reforming by 1-methylnaphthalene (1MN)**



- **1MN tentatively deactivates reforming reaction.**
- **Activity recoverable after 1MN removal.**
- **Performance improves with T increases.**
- **O_2/C & H_2O/C have limited impact.**

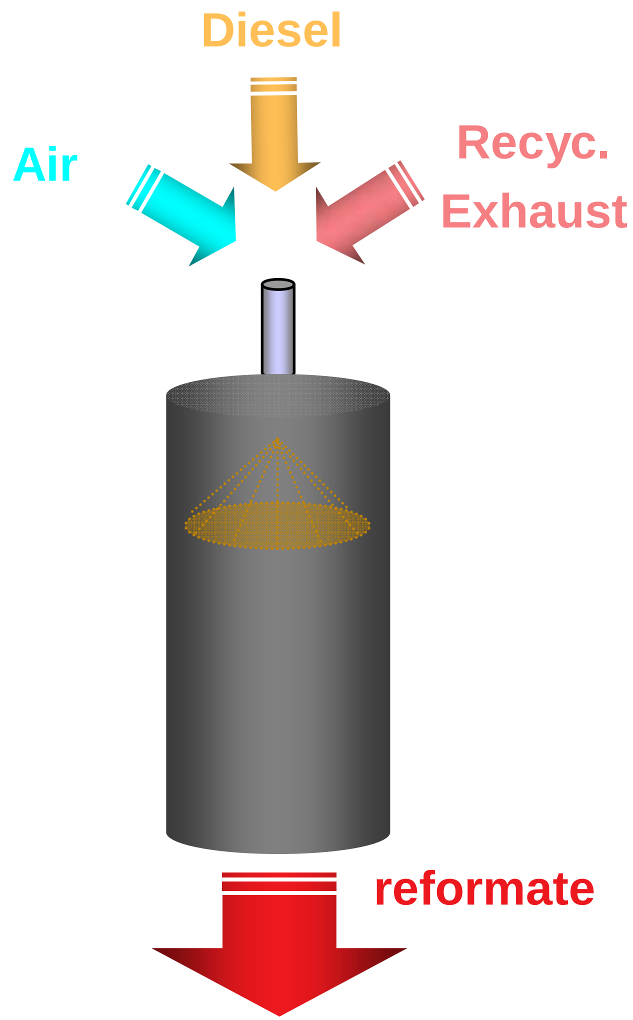
Diesel ATR Catalyst Development – Summary

- **Ru doped chromites and aluminites demonstrate excellent catalytic reforming activities comparing with Rh based catalysts.**
- **Active catalysts are the perovskites containing Ru at B site with high oxygen vacancy and high surface area.**
- **The sulfur tolerance of the catalyst can be improved through higher operating temperature. Good catalytic stability was demonstrated in 100 hour aging test.**
- **Polyaromatics can temporarily deactivate catalytic activity thus needs to be addressed.**

Diesel Fuel Mixing Study

The Challenges Facing Fuel Mixing

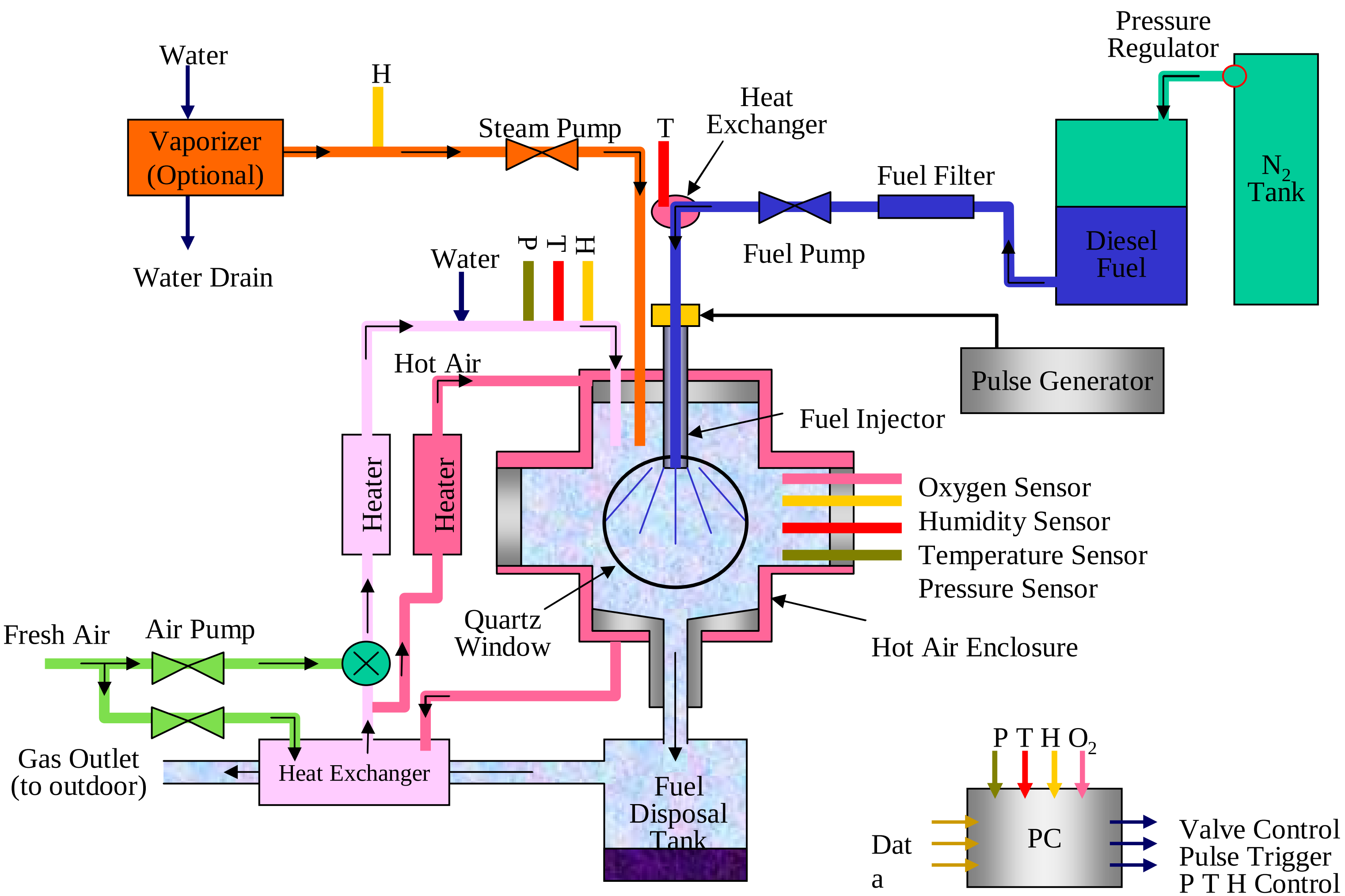
- Diesel fuel cannot be evaporated
- Incomplete mixing creates “hot spots” on the catalyst and leads to coke formation
- Pre-heating the air appears to prevent pre-ignition



Approach to Mixing Challenge

- **Joint effort between ANL and International Truck and Engine Corporation (ITEC)**
  - ITEC provides diesel-fuel injectors and fuel-injection control system
  - ANL will establish a test facility, develop a fuel/exhaust-gas mixing system, and conduct tests to evaluate the ANL autothermal reforming process.

Fuel-air-steam Mixing Facility



ITEC Diesel Fuel Injector

- Pulsed injection with pulse rate of
  10 ~ 70 Hz (500 ~ 4000 rpm for 4-cylinder engine)
- Injection duration
  Below 1 ms at idle to 20 ms at high load
- Injection nozzles
  6 holes around
- Fuel injection rate

Peak Torque:	105 mm^3/stroke at 240 bar and 600 rpm
Idle Single Shot	9.2 mm^3/stroke at 45 bar and 600 rpm

Fuel Injection Test Chamber

Test Matrix

- **Test variables**
  - Exhaust-gas-fuel ratio (O/C : 0.4, Steam/C : 1.0)
  - Exhaust-gas temperature (300 deg. C)
  - Exhaust-gas water content (10%)
  - Mixing configuration
- **Proposed measurements**
  - Flow rates (exhaust gas and fuel)
  - Temperatures (fuel, exhaust-gas, and mixing region)
  - Fuel mist characterization
  - Carbon deposit
  - Humidity
  - Pressure

Acknowledgements

- **This work was supported by the U.S. Department of Energy, Office of Fossil Energy –Solid State Energy Conversion Alliance (Program Manager, Norman Holcombe) and Office of Energy Efficiency and Renewable Energy –FreedomCar& Vehicle Technologies (Program Manager, Sid Diamond).**

- **Thanks to the technical support by**
  - -CécileRossignol
  - -Mike Schwartz
  - -JameelShihadeh
  - -Martin Bettge
  - -Jeremy Kropf